



INSTITUTE FOR ENGINEERING THERMODYNAMICS
Chairman: Prof. Dr.-Ing. Stefan Will

Laboratory course report
**Optical Diagnostics in Energy and Process Engineering -
Application of TDLAS**

Authors: Maximilian Köhler (23176975)
Energy technology (Master)
Jean-Pascal Lafleur (23266512)
Mechanical engineering (Master)

Supervisor: M.Sc. Benjamin Klevansky

Group: 1

Execution date: January 23, 2024

Submission date: February 07, 2024



Contents

| | |
|--|-----|
| List of Figures | III |
| List of Tables | IV |
| 1 Introduction | 1 |
| 2 Theoretical basics | 2 |
| 3 Experimental setup | 4 |
| 3.1 Measurement setup and preparations | 4 |
| 3.2 Post-processing strategy | 5 |
| 4 Results | 8 |
| 5 Summary | 13 |
| Bibliography | V |

List of Figures

| | | |
|-----|--|----|
| 2.1 | Components and working principles of a laser | 2 |
| 2.2 | Tunable littrow laser arrangement | 3 |
| 3.1 | Experimental setup of the TDLAS measurement | 4 |
| 3.2 | Evaluation procedure diagram | 6 |
| 4.1 | Calibration factor over wavelength | 8 |
| 4.2 | Relative absorption spectra | 9 |
| 4.3 | Comparison of origin, transmitted and absorbed signals | 10 |
| 4.4 | Extinction and extinction factor over the spectrum | 11 |

List of Tables

4.1 Extinction and extinction factor results 12

1 Introduction

A rather simple, but yet effective optical technique for analyzing and determining the species, concentration, pressure, temperatures or density of materials is the Tunable Laser Absorption Spectroscopy (TDLAS). This optical method relies on the specific and characteristic light absorption of substances. It used a manipulated laser to generate a bandwidth of wavelength. With that one can have a look at complete spectra and the absorption behavior over them. It can be grouped into the laser spectroscopy methods. Specific applications are particle technology (determining particle densities or concentrations), environmental technology, material composition or other technical fields.

This paper is documenting and discussing an experiment, more specifically a laboratory course, with this measurement method. It is carried out at the Institute for Engineering Thermodynamics (LTT) of the FAU Erlangen-Nuremberg at its site in Erlangen-Tennenlohe.

The assignment, description of the equipment and procedure and further details about the Lab Course are described in the given handbook [1].

2 Theoretical basics

The following theoretical basics are summarized from the standard literature in optics [2]–[5] and more specifically Raman application [6], [7]. In addition the given handbook [1] is used as well.

The central principle TDLAS relies on, is the absorption of light. Next to absorption, there are more processes which can occur with an incoming photon or light beam, such as scattering, reflection, or diffraction. In this case the focus is only on the first. Absorption of photons, or electromagnetic radiation, can only occur, if the struck molecule matches the energy of the photon with the energy difference of two of its discrete energy levels. This is called the resonance condition. This energy can be expressed as

$$E = h \cdot \nu.$$

The absorption can be visualized when hitting the molecule with a bandwidth light source. When analyzing the spectrum after the interaction, there are gaps or narrow dark bars occurring in the spectrum. Smaller molecules tend to form discrete lines, larger molecules more washed out reduction of the light spectrum. When using lower energy containing infrared radiation (IR), more vibrational or rotational states in the electronic ground state of the molecule are penetrated. In comparison the usage of higher energy contain ultra violet light, the electronic ground state can be elevated as well, and other unwanted effects such as fluorescence can occur. With the IR absorption, the generated spectrum and its gaps are acting like a fingerprint for the molecule. Species determination is easily possible that way.

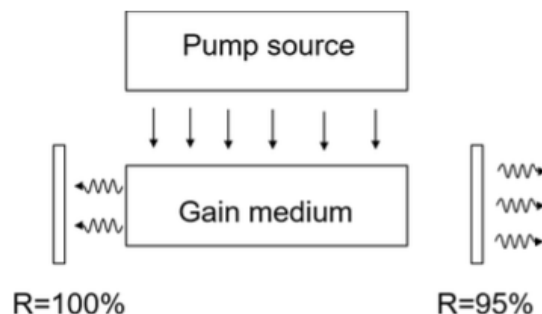


Figure 2.1: Simple working principle of a laser; simplified components [1]

To precisely analyse the absorption spectra, a bandwidth light source is not pleasant to use. A better way is the usage of a wavelength tunable laser. This can e.g. be achieved with a

Littrow laser arrangement (see Figure 2.2), like in this experiment. This arrangement allows a tunable output wavelength through a variable placement of a grating, thus realised through an easy to control electrical motor. The diffraction grating reflects the first diffraction order of the laser beam back and forms a standing wave. It is used with its easy positioning for creating the needed amplification (the basic laser principle is sketched in Figure 2.1). After reaching the laser threshold, the laser beam is coupled into a glass fibre and guided to the experimental setup. As a pump source a laser diode is utilized. The emitted basis wavelength is further tunable through the diode current and the temperature.

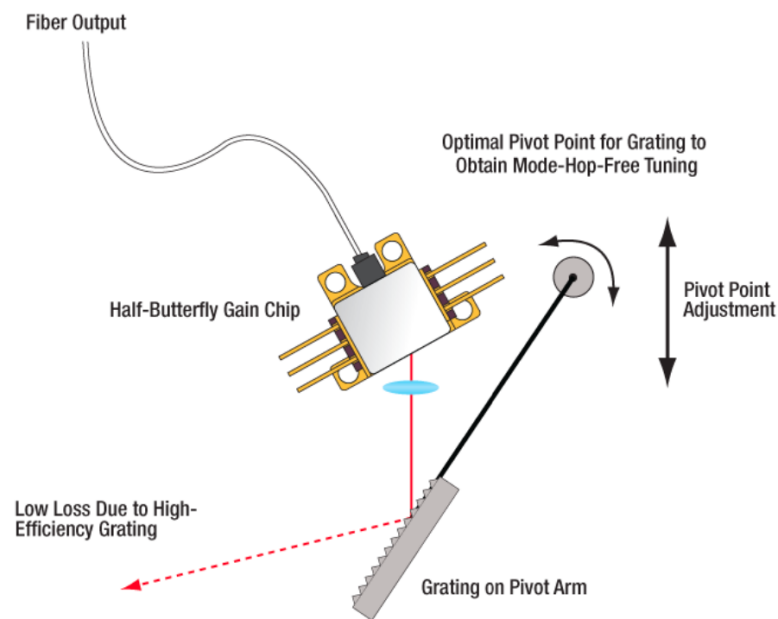


Figure 2.2: Tunable littrow laser arrangement [1]

3 Experimental setup

Following chapter shall describe the used experimental setup. The strategy of the data evaluation and result calculation shall be explained.

3.1 Measurement setup and preparations

A scheme of the measurement setup is illustrated in Figure 3.1. Controlling the whole setup, mainly the Littrow laser system and the chopper, and reading out the oscilloscope for data saving, is a computer. The laser signal is generated with a tunable diode laser setup (see Figure 2.2) for generating a defined bandwidth (between 1891 nm and 2022 nm) of wavelengths (see chapter 2 for a functional description). This signal is split into two beams and measurement paths. The chopper is acting as a pulser, so that the substance molecules and the photo diodes can relax and deexcite between the absorption processes. Between the chopper and the photodiode the probe is placed. After an intensification of the signal, it is read out with an oscilloscope. As a consequence the measurement is transmittive.

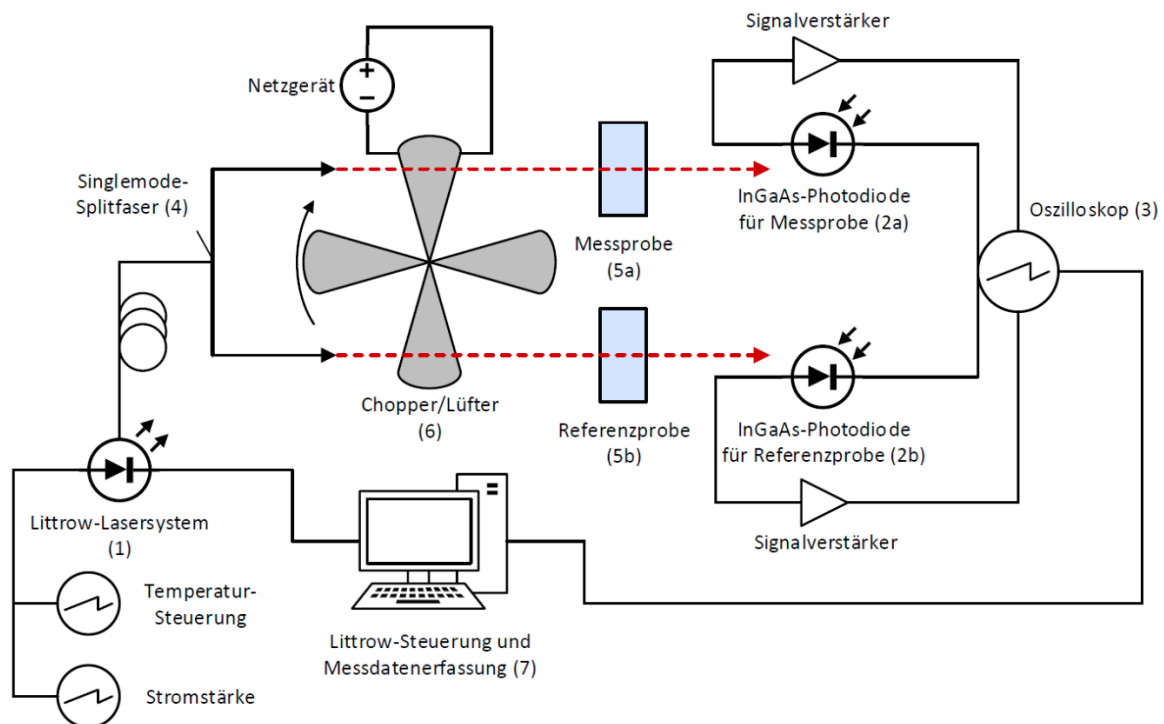


Figure 3.1: Experimental setup of the TDLAS measurement [1]

The procedure of the measurement is like following, whereas the laboratory script [1] is giving more detailed information.

1. Starting up sequence

For starting up the experiment, the laptop has to be boot up and the necessary software has to be started. Further, the control devices and operating temperatures have to be checked, such as laser temperature, laser current and voltage supply.

2. Calibration of the two measurement channels

Cuvettes have to be removed and a calibration measurement at each wavelength over both measurement paths A and B is needed. The calibration factor KF is calculated to normalize both signal pathways (especially the photodiodes). This step makes both pathways comparable.

3. Absorption spectrum measurement

As last step, the actual measurement of both species is carried out. Pathway A is used for acquiring the absorption spectrum of the species, path B is used with an empty cuvette as a reference measurement. Important to note is the dark signal of both channels.

3.2 Post-processing strategy

Starting off with the raw signals from the A/D-converter, the signal has to be corrected and normalized. Due to known and discussed effects of dark signals and different signal intensities from photo diodes, e.g. from differences out of manufacturing, two calibration steps have to be carried out. The dark signal must be subtracted from the general intensity (following Equation 3.1), the two channels have to be calibrated to each other with the help of an wavelength dependent calibration factor KF (see Equation 3.2).

$$I_{\text{measurement}} = I_{\text{photodiode}} + I_{\text{dark}} \quad (3.1)$$

$$KF(\lambda) = \frac{I(\lambda)}{I_0(\lambda)} \quad (3.2)$$

The calibration has to be considered for each discrete wavelength, the dark signal is uniformly relevant over the complete spectrum.

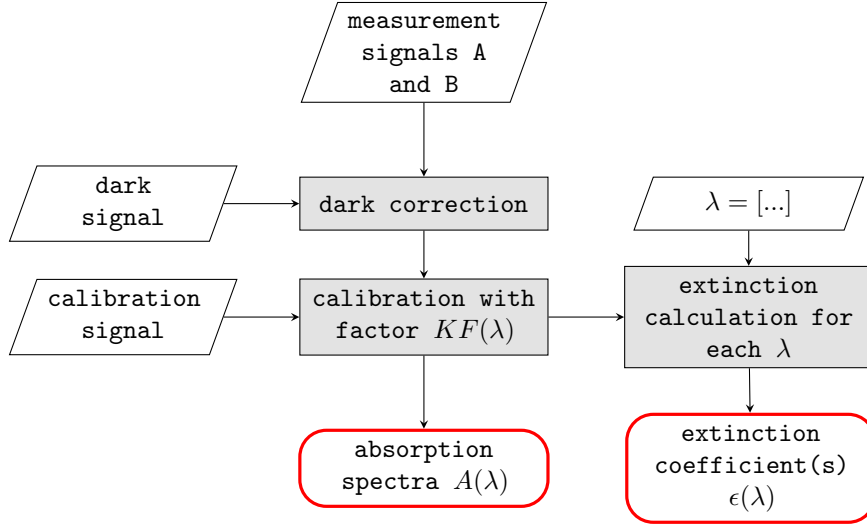


Figure 3.2: Evaluation procedure diagram

Since the Transmission ratio T , depending on the laser shot intensity I_0 and the transmitted intensity I is given through

$$T = \frac{I}{I_0}$$

and the Absorption ratio with the subtraction of T from one, we can state:

$$A = 1 - \frac{I}{I_0}$$

Further taking into account both calibration steps, we can develop as Absorption spectra

$$A(\lambda) = 1 - \frac{(I_A - I_{\text{dark}}) \cdot KF(\lambda)}{I_B - I_{\text{dark}}}. \quad (3.3)$$

Determining the extinction coefficient is possible through rearranging Lambert-Beer's law (see Equation 3.4). Important to note is the wavelength and temperature dependency of this coefficient, although the last one is kept constant at this experiment. Selected for evaluation of $\epsilon(\lambda)$ are following wavelengths:

$$\lambda = [1906, 1950, 1977, 2003] \text{ nm}$$

$$\epsilon(\lambda) = \frac{\log(I_0) - \log(I)}{c \cdot d} \quad (3.4)$$

The evaluation procedure is shown in Figure 3.2. For this calculation following parts have to be recorded during the experiment:

1. Measurement signal of the species at every wavelength
2. Reference spectrum at every wavelength
3. Dark signal before the measurement
4. Simultaneous signal of path A and B at every wavelength

4 Results

The following chapter shall present the preparations and results from the TDLAS experiment. A discussion of possible errors and improvements shall be given afterward.

Starting with the calibration measurement to normalize both pathways A and B, the calibration curve is plotted in Figure 4.1. The calibration factor KF is wavelength-dependent and concerns the discrete measurement plotted with discrete data points. The values pend around 0.75 and 0.95, thus are similar, but yet different on each wavelength. This can result through a different quantum efficiency for the discrete wavelengths or through disturbing substances in the measurement path.

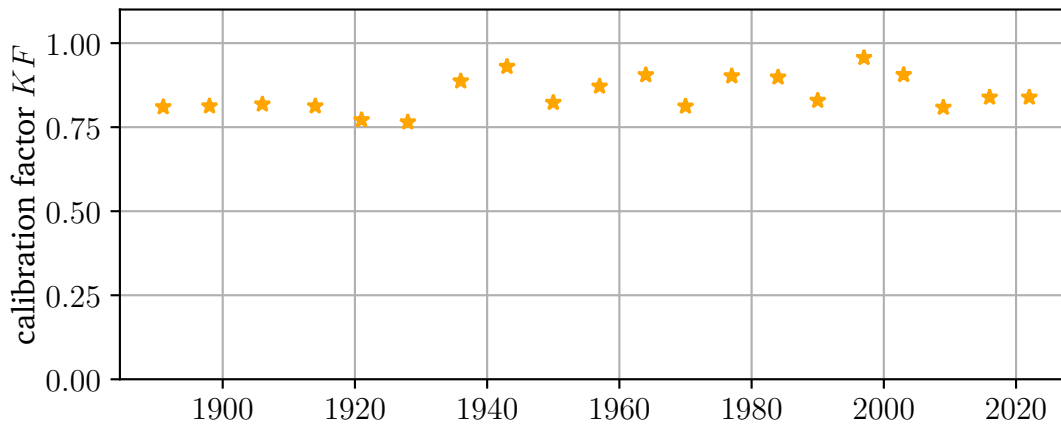


Figure 4.1: Calibration factor over wavelength

The absorption spectra for DMSO and EtSO₄ are shown in Figure 4.2. The wavelengths for determination of the extinction and extinction coefficient are marked as vertical, purple, and dashed lines. It can be observed, that both substances have similar behavior in terms of which wavelengths are more and less absorbed, due to the spectrum shape. It can be added, that *DMSO* is significantly less absorption active and thus transmits more light. The absolute transmission and absorption are illustrated in Figure 4.3, while the original laser signal is added. Noticeable is however the very high absorption rate of EtSO₄ in the wavelength region around 1940 nm. Another abnormality is the not smooth but rather jumping intensity of the laser incoming, as well transmission and absorption signal. Reasons for that can rely on the laser itself, having more or less efficiencies dependent on the emitted wavelength. Another explanation could be the quantum efficiency of the photodiodes or disturbing substances like fingerprints on the surface of the cuvette.

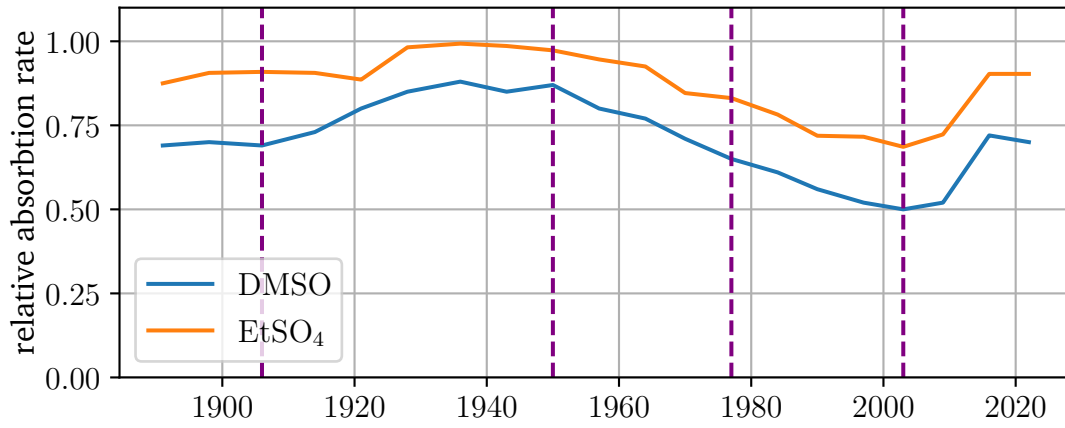


Figure 4.2: Relative absorption behavior of DMSO and EtSO₄ over the analyzed spectrum

The extinction E and the extinction factor are plotted in Figure 4.4, and the discrete values for the desired wavelengths are shown in Table 4.1. As seen in Figure 4.3, the absorption is very high in the region between 1900 nm and 1960 nm, especially for EtSO₄. The order of the remaining transmission signal is between 2 and 7, while the standard deviation for the dark signal is around 1 (dark signal itself $15 \frac{\text{A}}{\text{mV}}$). This shows that this wavelength region is highly error-prone, especially for relative calculations. Improvements would be a higher laser power, or a smaller cuvette, resulting in a higher signal intensity.

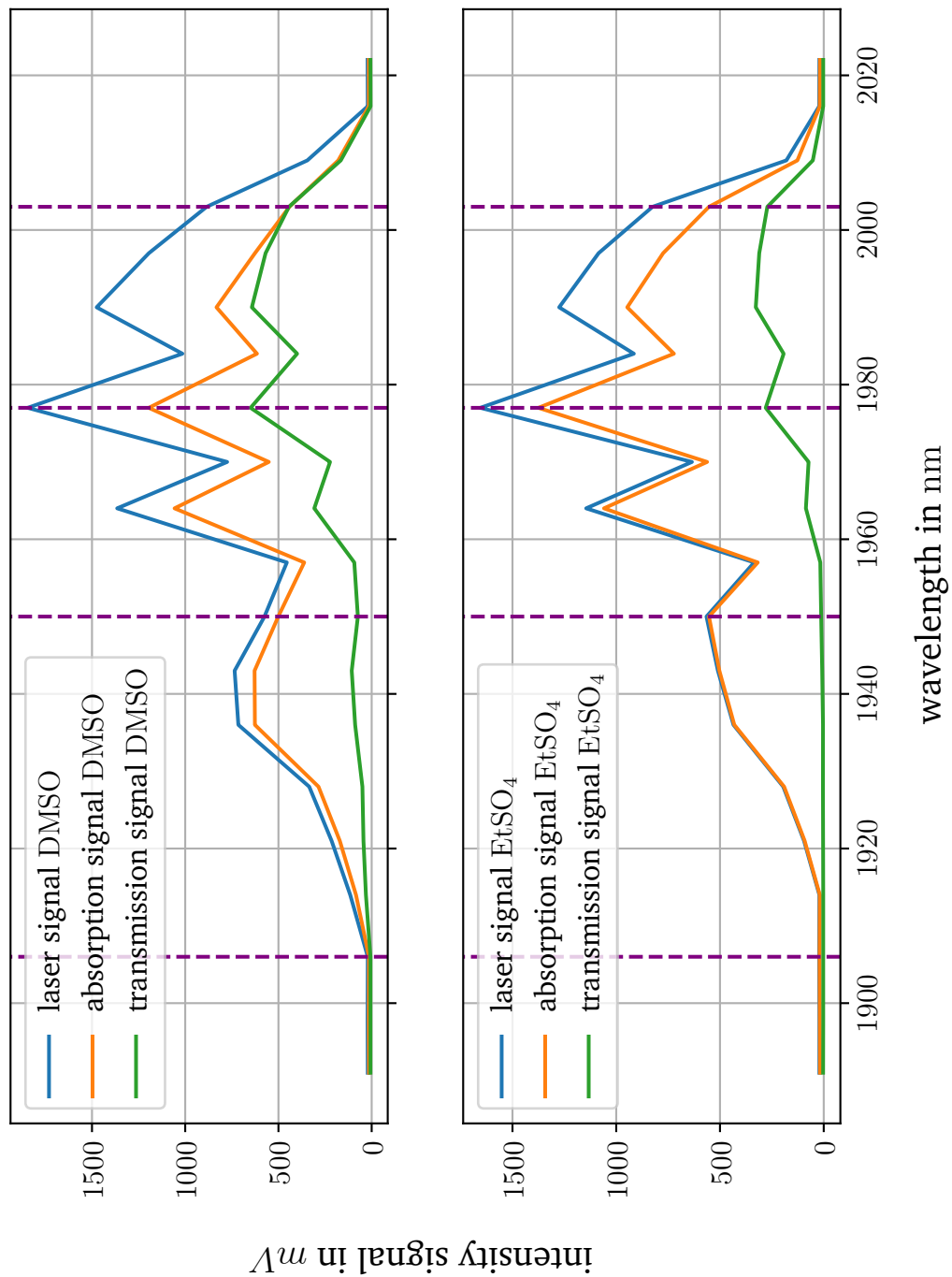


Figure 4.3: Comparison of laser signal intensity, transmission intensity, and absorption intensity; top for DMSO and bottom for EtSO₄ over the analyzed spectrum

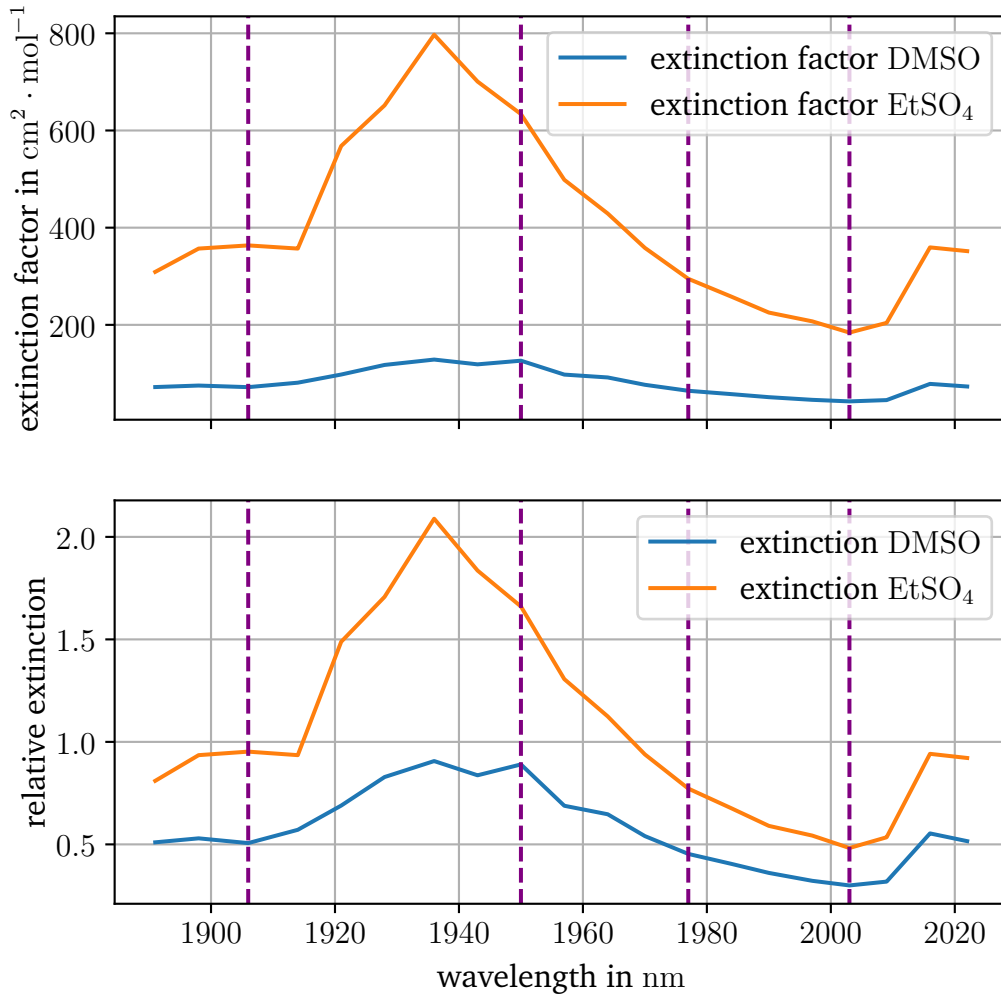


Figure 4.4: Extinction and extinction factor of DMSO and EtSO₄ over the analyzed spectrum; vertical, purple and dashed lines represent the desired wavelengths for the extinction calculation

Further regarding the three higher wavelength extinction calculations, it can be said, that they are directly located in the signal peaks of both transmission and incoming laser signal for EtSO₄, for DMSO this is the case for the upper two extinction factors. With this knowledge, it can be assumed that the relative errors are comparably low for the two relative extinctions and extinction factors at the wavelengths 1977 nm and 2003 nm.

Errors concerning the measurement channels can be stated as follows. In general, it can be said, that high signal intensities put small manufacturing defects into perspective. Also using the same equipment or signal pathways for as long as possible is beneficial for getting as little error as possible from the measurement.

1. The intensifiers have a deviation in their intensification rate

Table 4.1: Extinction and extinction factor at desired wavelengths for DMSO and EtSO₄

| wavelength in nm | extinction factor in $\frac{\text{cm}^2}{\text{mol}}$ | extinction |
|-------------------|---|------------|
| DMSO | | |
| 1906 | 72 | 0.51 |
| 1950 | 126 | 0.89 |
| 1977 | 64 | 0.45 |
| 2003 | 43 | 0.30 |
| EtSO ₄ | | |
| 1906 | 364 | 0.95 |
| 1950 | 634 | 1.66 |
| 1977 | 295 | 0.77 |
| 2003 | 184 | 0.84 |

This systematic error is similar to the cause for calibration of both measuring channels and thus is normally eliminated by the correction factor KF . However, when the difference between the intensifiers becomes large, the effect of the photodiode difference can be multiplied. In case of a large intensification of a larger signal of the CCD, the difference in signal becomes bigger and thus the calibration factor is very different from one. In case of a large intensification of the smaller signal, the error itself gets multiplied and large.

2. The intensity is near the intensity of the dark signal

The same effect can occur, as discussed in the previous paragraph for the very high absorption rate and resulting large relative error. When the dark signal and its standard deviation are getting bigger and in the range of the signal itself, very little signal intensity is left to interpret. This can then be (relatively) error-prone.

3. Fluctuating temperature of the experiment

With this last error, an increase in thermal noise over the measurement time due to the heating of the sensor or a signal shift from the specimen is considered. When the measurement frequency is high and the relaxation time low, heating can occur and thus a gain in thermal noise in the CCD. In the case of the specimen signal, a shift, intensification or decrease of the transmission signal could be observed.

5 Summary

This Tunable Diode Laser Absorption Spectroscopy (TDLAS) experiment introduced the basics of both absorption spectroscopy and tunable diode laser setups. It showed the strengths in an easy experiment setup with comparable large output, as well as its weaknesses in terms of error susceptibility, data interpretation, and needed knowledge.

It was possible to create a fingerprint-like absorption spectra resp. extinction measurement for two species, illustrate the benefits of simultaneous measurements and show influences on signal deviations or reductions.

Bibliography

- [1] B. Klevansky, *TDLAS – Tunable laser diode absorption spectroscopy*.
- [2] M. Born and E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th expanded ed. Cambridge ; New York: Cambridge University Press, 952 pp., ISBN: 978-0-521-64222-4 978-0-521-63921-7.
- [3] E. Hecht and E. Hecht, *Optik*, 4., überarb. Aufl. München Wien: Oldenbourg, 1116 pp., ISBN: 978-3-486-27359-5.
- [4] S. G. Lipson, H. S. Lipson, and D. S. Tannhauser, *Optik*. Berlin, Heidelberg: Springer Berlin Heidelberg : Imprint : Springer, ISBN: 978-3-642-59053-5.
- [5] H. Niedrig, Ed., *Optik: Wellen- und Teilchenoptik: Part 1* (Lehrbuch der Experimentalphysik / Bergmann; Schaefer 3, Part 1), 10. Auflage[Ausg. in 8 Bänden]. Berlin: de Gruyter, 668 pp., ISBN: 978-3-11-017081-8.
- [6] Herzberg and Huber, *Molecular Spectra and Molecular Structure. 4, Constants of Diatomic Molecules*, Ristampa anastatica. Berlin: Springer, ISBN: 978-1-4757-0963-6.
- [7] B. Schrader and D. Bougeard, *Infrared and Raman Spectroscopy: Methods and Applications*. Weinheim: VCH, ISBN: 978-3-527-61543-8.